QUANTUM RELATIONS IN PHOTO-ELECTRIC PHENOMENA

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For the past ten years I have been engaged with experiments which were designed for the sake of subjecting Einstein's photo-electric quantum-theory equation to searching experimental tests, and although I have at times thought that I had evidence which was irreconcilable with that equation, the longer I have worked and the more completely I have eliminated sources of error the better has the equation been found to predict the observed results. I shall present herewith the barest sketch of six consequences of that equation and their experimental verification. Preliminary reports on some of these results have already been made[1] and detailed reports will be found in forthcoming numbers of the *Physical Review*.

Einstein's equation[2] grew out of a semi-corpuscular quantum theory of radiation. The assumption was that light consists of bundles or 'quanta' of electromagnetic energy which shoot out explosively from the emitting body and travel through space as localized units until they are suddenly absorbed by the atoms of matter upon which they fall. The energy in each light-unit was assumed equal to $h\nu$, in which h is Planck's 'wirkungs-quantum' and ν is the frequency of the oscillator which emits the light. Upon absorption this energy was assumed to be transformed into the kinetic energy of an escaping negative electron whose energy of escape from a metal illuminated by light of frequency ν was thus given by $\frac{1}{2}mv^2 = h\nu - p$, in which p was the work necessary to separate the electron from the surface of the metal. The maximum energy of escape is measured by $(V_0 + K)e$ in which e is the electronic charge, K the contract EMF between the emitting plate and the opposed Faraday cylinder which catches the electron, and V_0 the potential difference which must be externally applied just to stop the photo-current to this cylinder. The assertions contained in the equation $\frac{1}{2}mv^2 = h\nu - p$ are that:

1. There is a definite maximum energy of electronic emission under the stimulation of a given frequency ν. (This has recently been denied by Ramsauer.[3])
2. There is a linear relation between V_0 and ν.
3. The slope of the $V_0\nu$ line multiplied by e is exactly Planck's 'h.'
4. The intercept of this $V_0\nu$ line on the ν axis is the frequency ν_0 at which the illuminated substance first becomes photo-sensitive.

5. The contact EMF between the illuminated plate and the Faraday cylinder is given by,

$$\text{Contact EMF} = \frac{h\nu_0 - h\nu'_0}{e} - (V_0 - V'_0),$$

in which ν_0 and ν'_0 are the frequencies at which the cylinder and the

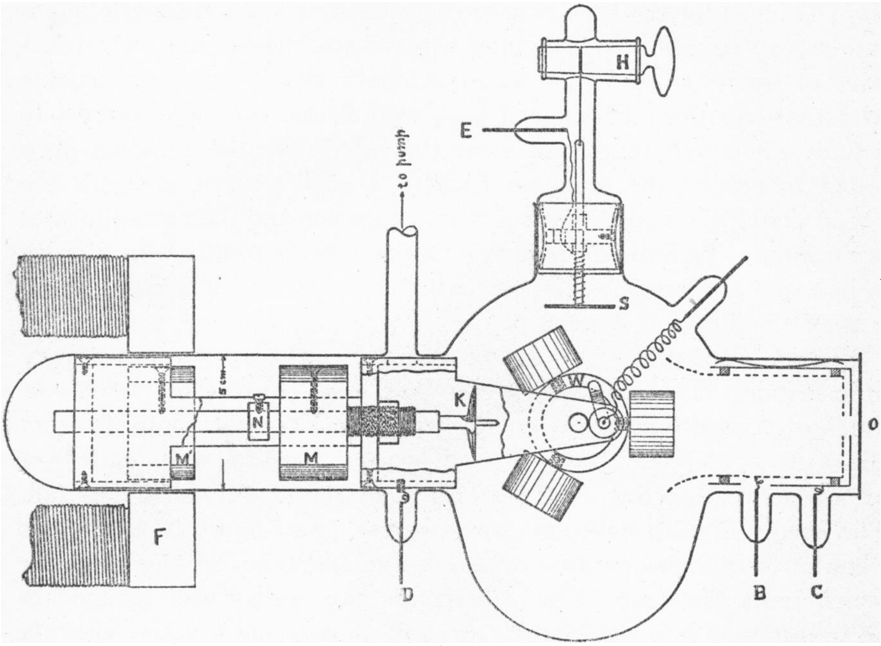

FIG. 1.

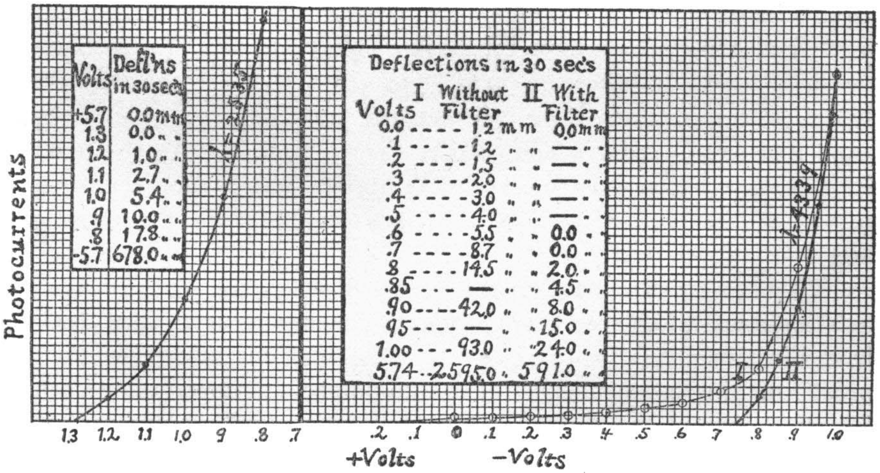

FIG. 2.

plate respectively first become photo-sensitive, and V_0 and V'_0 are the respective maximum potentials necessary to stop discharge into the cylinder from the plate and from another plate made from the substance of the cylinder.

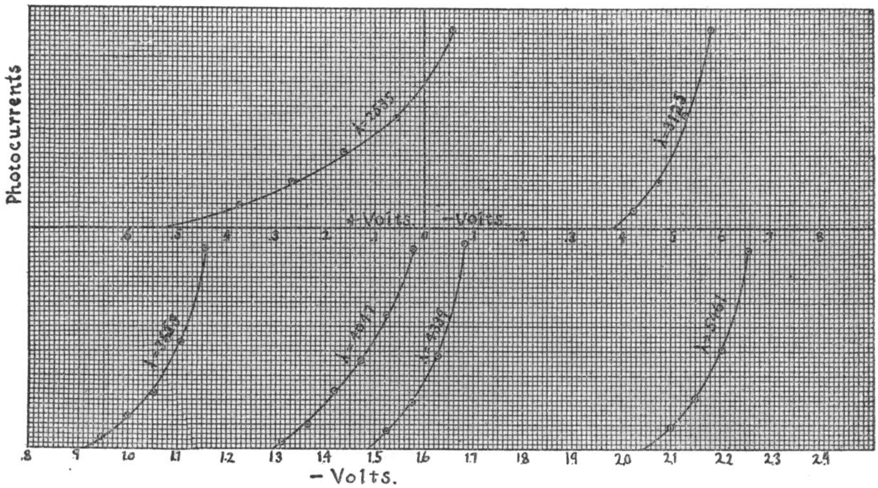

FIG. 3.

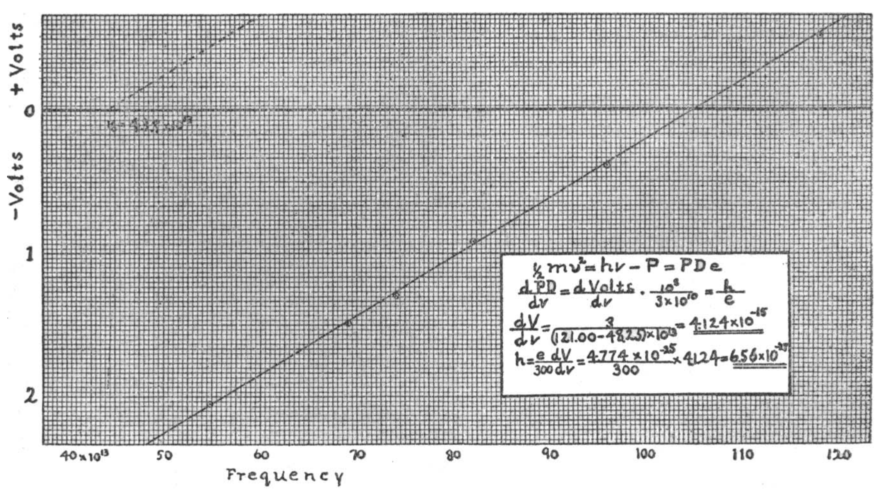

FIG. 4.

6. Contact EMF's are independent of temperature. This follows from Einstein's equation taken in connection with our now well confirmed proof[4] of the independence of photo-potentials upon temperature. Where, however, surface films cause variations with temperature of photo-potentials, there should be corresponding variations in contact EMF.

The experiments are made with a device shown in figure 1 by which clean new surfaces of potassium, sodium, and lithium can be produced by shaving in an extreme vacuum, and photo currents and contact EMF's

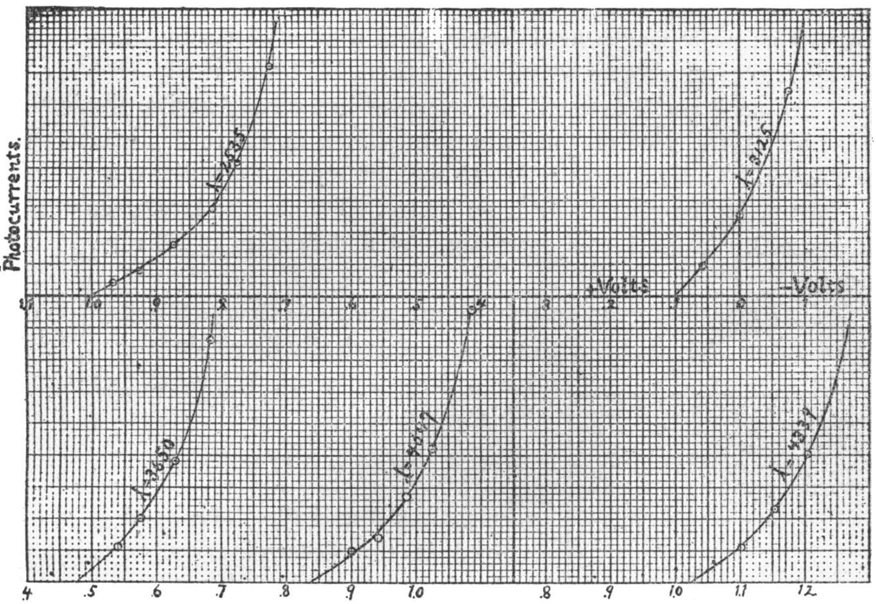

FIG. 5.

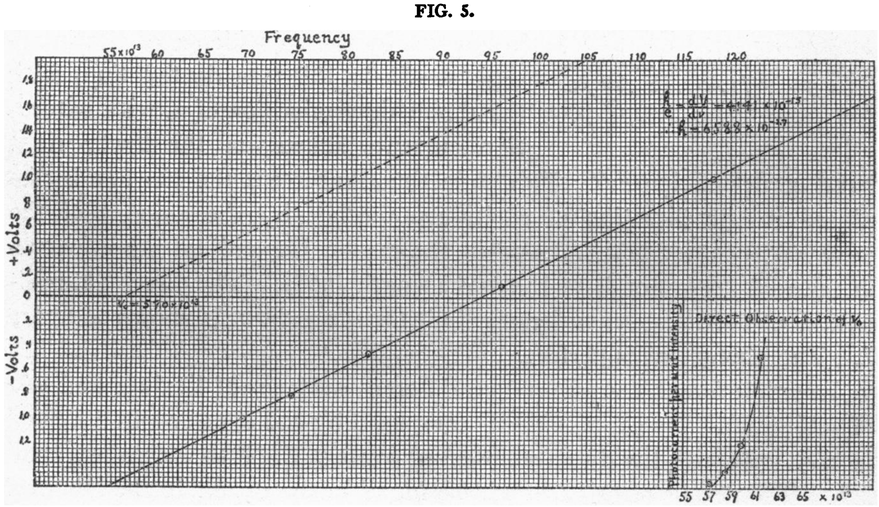

FIG. 6.

measured immediately thereafter. The tube has a projection toward the reader not shown in the diagram with the aid of which the wheel w may be rotated by means of an electromagnet similar to F and a third armature similar to M and M'.

The data on lithium shown in figure 2 seems to establish assertion 1, the difference between curves I and II taken with the mercury line 4339 and a Hilgar monochromator showing how the true shape (II) of the photo-current-potential curve was entirely falsified by a little stray short wave-length light (see I) until a filter of aesculin which cut out all waves of shorter wave-length then 4339 was used.

Assertions 2 and 3 are strikingly verified in figures 3 and 4, the latter of which is the plot of the intercepts shown in figure 3, against the frequency. These figures relate to measurements on sodium, in which the saturation currents were from 75 to 500 times the largest currents in figure 3. These latter correspond to a deflection of 80 mm. in 30 seconds.

Similar measurements on lithium are shown in figures 5 and 6. The mean value of Planck's h thus photo-electrically determined should not be in error by more than 0.5 per cent. This value is

$$h = 6.57 \times 10^{-27}$$

(see figures 4 and 6). The value of e involved in this determination of h is the author's value[5] 4.774×10^{-10}.

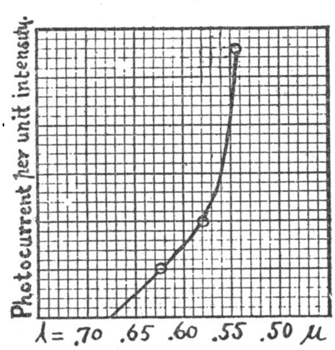

FIG. 7.

The correctness of assertion 4 is shown in figure 6 by the coincidence of the intercept $\nu_0 = 57.0 \times 10^{13}$ (see dotted line) with the direct determination of ν_0 with saturation currents shown on the lower right hand corner of figure 6. To obtain the ν_0 intercept the $V_0\nu$ line is displaced in the direction of positive potentials by the amount of the measured contact EMF. Also in the case of the sodium the ν_0 shown in figure 4 corresponds to the wave length 0.68μ. The direct determination of this long wave length limit for the sodium is shown in figure 7. The agreement is perfect.

Assertion 5 was tested for two different surfaces of lithium and one of sodium and the contact EMF computed by the equation in 5 agreed in each case with the directly observed contact EMF to within less than 2%. The details of this test will be found in the papers in the *Physical Review*.

Assertion 6 has not been tested in this work but Schottky[6] has recently measured the contact EMF's between white hot wires and cold cylinders and found results which agree, within the fairly wide limits of uncertainty, with the values which hold between the same metals at ordinary temperatures.

So far then as experiment has thus far gone, Einstein's equation seems to be an exact statement of the energies of emission of corpuscles under the influence of light waves.

Nevertheless the physical theory which gave rise to it seems to me to be wholly untenable. Be this as it may, however, the photo-electric results herewith presented constitute the best evidence thus far found for the correctness of the fundamental assumption of quantum theory, namely, the discontinuous or explosive emission of energy by electronic oscillators. They furnish the most direct and most tangible evidence which we yet have for the actual physical reality of Planck's *h*.

[1] R. A. Millikan, *Physic. Rev.*. Ser. 2, 4, 73 (1914); *Ibid.*, 6, 55 (1915).

[2] Einstein, *Ann. Physik.*, Ser. 4, 17, 132 (1905) and 20, 199 (1906).

[3] Ramsauer, *Ann. Physik.*, 45, 1120 (1914), also 45, 961.

[4] Millikan and Winchester, *Physic. Rev.*, 24, 16 (1906), and *Phil. Mag.*, Ser. 6, 14, 188 (1907).

[5] Millikan, *Physic. Rev.* 2, 143 (1913).

[6] Schottky, *Ann. Physik.*, 44, 1011 (1914).

THE CHEMICAL ACTIVITY OF THE IONS OF HYDROCHLORIC ACID DETERMINED BY ELECTROMOTIVE FORCE MEASUREMENTS

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The fact that the laws of perfect solutions which are conformed to by unionized or slightly ionized substances in dilute aqueous solutions are subject to large deviations in the case of largely ionized substances (salts, strong acids and bases) even at small concentrations makes it necessary, in the absence of any theoretical explanation of the deviations, to treat dilute solutions of these substances like concentrated solutions of other substances, namely, to determine experimentally the behavior of the separate substances, with the hope that this empirical study may then lead to generalizations. Now the most important characteristic of ionizing substances is the chemical activity which results from their ionization, or more specifically the (mass-action) effect which their ions exercise in determining chemical equilibria. This effect in the case of theoretically perfect solutes is proportional to the concentration of the ions; but in the case of deviating solutes there must be substituted